Inhomogeneous Steady States of Diffusion-Limited Coalescence, $A + A \rightleftharpoons A$

Daniel ben-Avraham*
Physics Department, and Clarkson Institute for Statistical Physics (CISP), Clarkson University, Potsdam, NY 13699-5820

We study the steady state of diffusion-limited coalescence, $A + A \rightleftharpoons A$, in the presence of a trap and with a background drift. In one dimension this model can be analyzed exactly through the method of inter-particle distribution functions (IPDF). Because of the irreversible trap the steady state of the system is a non-equilibrium state. An interesting phase transition, controlled by the drift away from the trap, takes place: from a non-trivial steady state, when the drift is weak, to a trivial steady state (the vacuum), as the drift increases beyond some critical point. Surprisingly, regardless of the drift strength, the computed IPDF resembles that of an homogeneous *equilibrium* system, without the trap. We suggest that this is due to "shielding": the particle nearest to the trap shields the remaining particles from the effects of the trap. Finally, we compare the exact solution to that of a reaction-diffusion equation, and we determine the optimal values of the appropriate rate coefficients.

I. INTRODUCTION

Non-equilibrium kinetics of diffusion-limited reactions has been the subject of much recent interest [1–7]. In contrast to equilibrium systems—which are best analyzed with standard thermodynamics—or reaction-limited processes—whose kinetics is well described by classical rate equations [8,9]—there is no general approach to non-equilibrium, diffusion-limited reactions.

In this paper we study a diffusion-limited coalescence process in one dimension: $A + A \rightleftharpoons A$, which yields itself to *exact* analysis [10–21]. We show that a solution is possible even in the presence of background drift, and in the presence of a trap; when in the long-time asymptotic limit the stationary state of the system is a *nonequilibrium* state. The drift field controls an interesting phase transition in the steady state of the system: The size of the depletion zone next to the trap increases as a function of the drift away from the trap. Beyond a certain critical drift strength, the only possible stationary state is the vacuum (an empty lattice, with no particles).

Our analysis of the steady state yields the surprising result that the distance between a given particle and the nearest particle to its right (the "forward" IPDF) is exactly the same as in equilibrium, even in the presence of a trap, and independently of the drift! We suggest that this is due to a "shielding" effect: the particle nearest to the trap shields the rest of the particles from the effect of the trap. The trap and the drift influence only the distance between the trap and the nearest particle to the trap—all other particles remain unaffected.

Finally, we use the coalescence model with a trap to study the applicability of reaction-diffusion equations. Reaction-diffusion equations are the most common approximation method in the study of diffusion-limited processes. Our system is a rare example where (in the absence of drift) the stationary solution of the relevant reaction-diffusion equation may be found in closed form. We explore in what ways the reaction-diffusion equation is approximate, by comparing its results to the exact solution of the IPDF method. The comparison also allows us to determine the optimal rate constants of the reaction-diffusion equation in a straightforward manner. Normally, this feat requires a renormalization group analysis.

The rest of this paper is organized as follows. In Section II we present a lattice model of diffusion-limited reversible coalescence, along with the exact method of analysis; the method of Empty Intervals, also known as the method of Inter-Particle Distribution Functions (IPDF). The stationary *equilibrium* state in a homogeneous infinite system, needed for comparison with the trap, is analyzed and summarized in Section III. In Section IV, a trap is introduced and the resulting stationary state is explored. The exact solution includes a description of the dynamical phase transition in the stationary kinetics of the system, brought about by the background drift. The explanation to the surprising result that the IPDF of the system with a trap is homogeneous (and exactly the same as in equilibrium) is presented in Section V. Last, in Section VI we compare the exact solution for the case of non-biased diffusion (zero drift) to that of the corresponding reaction-diffusion equation. Our goal is to show in what ways the latter is an approximation, and to devise strategies to find out appropriate rate coefficients. We conclude with a discussion and open questions in Section VII.

*e-mail: qd00@polaris.clarkson.edu

II. REVERSIBLE COALESCENCE

Our model [10–12] is defined on a one-dimensional lattice of lattice spacing a. Each site is in one of two states: occupied by a particle A ($\bullet$), or empty ($\circ$). Particles hop randomly to the nearest neighbor site on their right (left), at rate $D/a^2 + u/2a$ ($D/a^2 - u/2a$). Thus, in the continuum limit of $a \to 0$, the particles undergo diffusion with a diffusion constant D, and with a uniform background drift velocity u. A particle may give birth to an additional particle, into a nearest neighbor site, at rate v/a (on either side of the particle) [22]. If hopping or birth occurs into a site which is already occupied, the target site remains occupied. The last rule means that coalescence, $A + A \to A$, takes place *immediately* upon encounter of any two particles. Thus, the system models the diffusion-limited reaction process

$$A + A \rightleftharpoons A \; . \tag{1}$$

The dynamical rules of the model are illustrated in Fig. 1.

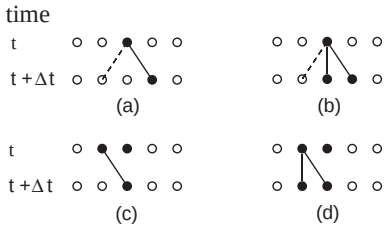

Figure 1. Reaction rules: (a) diffusion; (b) birth; and coalescence, (c) following diffusion, and (d) following a birth event. The dotted lines in (a) and (b) indicate alternative target sites. In (a), the rate of the two possibilities differ due to the drift.

An exact treatment of the problem is possible through the method of Empty Intervals, known also as the method of Inter-Particle Distribution Functions (IPDF). The key concept is $E_{n,m}(t)$—the probability that sites $n, n+1, \cdots, m$ are empty at time t. The probability that site n is occupied is

$$\text{Prob(site } n \text{ is occupied)} \equiv \text{Prob}(\overset{n}{\bullet}) = 1 - E_{n,n} \; . \tag{2}$$

The event that sites n through m are empty (prob. $E_{n,m}$) consists of two cases: site $m+1$ is also empty (prob. $E_{n,m+1}$), or it is occupied. Thus the probability that sites n through m are empty, but site $m+1$ is occupied is

$$\text{Prob}(\overset{n}{\circ} \cdots \overset{m}{\circ} \bullet) = E_{n,m} - E_{n,m+1} \; , \tag{3}$$

and, likewise,

$$\text{Prob}(\bullet \overset{n}{\circ} \cdots \overset{m}{\circ}) = E_{n,m} - E_{n-1,m} \; . \tag{4}$$

With this in mind, one can write down a rate equation for the evolution of the empty interval probabilities:

$$\begin{aligned}
\frac{\partial E_{n,m}}{\partial t} &= (\frac{D}{a^2} + \frac{u}{2a})(E_{n,m-1} - E_{n,m}) \\
&-(\frac{D}{a^2} - \frac{u}{2a})(E_{n,m} - E_{n,m+1}) \\
&-(\frac{D}{a^2} + \frac{u}{2a})(E_{n,m} - E_{n-1,m}) \\
&+(\frac{D}{a^2} - \frac{u}{2a})(E_{n+1,m} - E_{n,m}) \\
&-\frac{v}{a}[(E_{n,m} - E_{n,m+1}) + (E_{n,m} - E_{n-1,m})] \; .
\end{aligned} \tag{5}$$

For example, the first term on the r.h.s. of Eq. (5) accounts for the increase in $E_{n,m}$ when the particle at the right edge of $\overset{n}{\circ} \cdots \circ \overset{m}{\bullet}$ hops to the right and the sites $n, \ldots, m$ become empty; the second term denotes the decrease in $E_{n,m}$ when a particle at $m+1$ hops to the left into the empty interval $n, \ldots, m$, and so on.

Eq. (5) is valid for $m > n$. The special case of $m = n$ corresponds to $E_{n,n}$—the probability that site n is empty. It is described by the equation

$$\begin{aligned}
\frac{\partial E_{n,n}}{\partial t} &= (\frac{D}{a^2} + \frac{u}{2a})(1 - E_{n,n}) \\
&-(\frac{D}{a^2} - \frac{u}{2a})(E_{n,n} - E_{n,n+1}) \\
&-(\frac{D}{a^2} + \frac{u}{2a})(E_{n,n} - E_{n-1,n}) \\
&+(\frac{D}{a^2} - \frac{u}{2a})(1 - E_{n,n}) \\
&-\frac{v}{a}[(E_{n,n} - E_{n,n+1}) + (E_{n,n} - E_{n-1,n})] \; .
\end{aligned} \tag{6}$$

Comparison with Eq. (5) yields the boundary condition:

$$E_{n,n-1} = 1 \; . \tag{7}$$

The fact that the $\{E_{n,m}\}$ represent *probabilities* implies the additional condition that

$$E_{n,m} \geq 0 \; . \tag{8}$$

Finally, if the system is not empty then

$$\lim_{\substack{n \to -\infty \\ m \to +\infty}} E_{n,m} = 0 \; . \tag{9}$$

In many applications, it is simpler to pass to the continuum limit. We write $x = na$ and $y = ma$, and replace $E_{n,m}(t)$ with $E(x, y; t)$. Letting $a \to 0$, Eq. (5) becomes

$$\frac{\partial E}{\partial t} = D(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2})E - (u+v)\frac{\partial E}{\partial x} - (u-v)\frac{\partial E}{\partial y} \; , \tag{10}$$

with the boundary conditions,

$$E(x, x; t) = 1 \; , \tag{11}$$

$$E(x, y; t) \geq 0 \; , \tag{12}$$

$$\lim_{\substack{x \to -\infty \\ y \to +\infty}} E(x, y; t) = 0 \; . \tag{13}$$

The concentration of particles is obtained from the continuum limit of Eq. (2), together with Eq. (11):

$$c(x,t) = -\frac{\partial E(x,y;t)}{\partial y}|_{y=x} \ . \tag{14}$$

The conditional joint probability for having particles at n and m but none in between, is (Fig. 2)

$$\begin{aligned} P_{n,m}(t) &= \mathrm{Prob}(\overset{n}{\bullet}\circ\cdots\circ\overset{m}{\bullet}) \\ &= E_{n+1,m-1} - E_{n+1,m} - E_{n,m-1} + E_{n,m} \ , \end{aligned} \tag{15}$$

which in the continuum limit becomes

$$P(x,y;t) = -\frac{\partial^2 E(x,y;t)}{\partial x\,\partial y} \ . \tag{16}$$

From P we can compute the IPDF. The "forward" IPDF, *i.e.*, the probability that given a particle at x the next nearest particle *to its right* is at y, is

$$p(x,y;t) = c(x,t)^{-1} P(x,y;t) \ . \tag{17}$$

Likewise, the "backward" IPDF—the probability that given a particle at y the next nearest particle *to its left* is at x—is

$$q(x,y;t) = c(y,t)^{-1} P(x,y;t) \ . \tag{18}$$

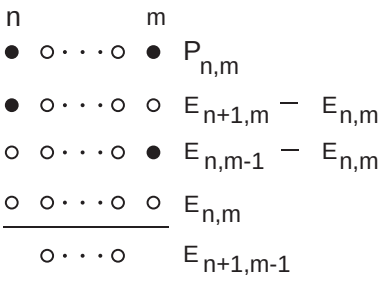

Figure 2. Discrete IPDF: $E_{n+1,m-1}$ consists of four events, listed above the "total" line. In this way one can find $P_{n,m}$—the only remaining unknown.

III. THE EQUILIBRIUM STATE

We now derive the steady state solution of Eq. (10), with the boundary conditions (11) – (13). It proves useful to change variables: $\eta = x + y$, and $\xi = y - x$. ξ represents the length of the intervals, and η represents their location (the center of the interval is at $\eta/2$). In these new variables, the stationary limit of Eq. (10) becomes

$$0 = (\frac{\partial^2}{\partial\eta^2} + \frac{\partial^2}{\partial\xi^2})E - \omega\frac{\partial}{\partial\eta}E + \gamma\frac{\partial}{\partial\xi}E \ , \tag{19}$$

where we have used the shorthand notation $\omega \equiv u/D$ and $\gamma \equiv v/D$.

Because the background drift is homogeneous, we expect the solution to be translationally invariant, that is, the probability of empty intervals should depend only on their length but not upon their location: $E = E(\xi)$. E then satisfies a simple ODE; $d^2E/d\xi^2 - \gamma dE/d\xi = 0$, whose solution (in view of the boundary conditions) is

$$E_{eq} = e^{-\gamma(y-x)} \ . \tag{20}$$

This corresponds to the particle concentration (Eq. 14)

$$c_{eq} = \gamma = \frac{v}{D} \ . \tag{21}$$

The subscript "eq" emphasizes the fact that here the stationary solution is an *equilibrium* solution. This is to be expected because all the microscopic rules involved are reversible. Notice that the equilibrium solution is independent of the drift. The effect of the drift is to impart the whole system a uniform background velocity, u, which in fact may be eliminated through a Galilean transformation.

We can test that the distribution of particles is indeed an equilibrium distribution, by working backwards. At equilibrium the particles ought to be distributed randomly, independently from each other—a state of maximum entropy. Suppose that the particle concentration is γ, then the probability that there are no particles in an infinitesimal interval of length $\Delta\xi$ is $(1-\gamma\Delta\xi)$. Since the particles are uncorrelated, the probability that a finite interval of length $\xi = y - x$ is empty is then $(1-\gamma\Delta\xi)^{\xi/\Delta\xi}$. In the limit $\Delta\xi \to 0$, one recovers the equilibrium empty interval probability, Eq. (20).

Finally, we can work out the IPDF. Using Eqs. (16) – (18), (20), and (21), we find the Poisson distribution:

$$p_{eq}(x,y) = q_{eq}(x,y) = \gamma e^{-\gamma(y-x)} \ . \tag{22}$$

Again, this can be obtained, independently, from an analysis of uncorrelated, randomly distributed particles.

IV. STEADY STATE WITH A TRAP

The equilibrium solution, Eq. (20), is not the only solution to Eq. (19). Another trivial solution is the "vacuum" state; $E(x,y) = 1$. It represents a completely empty system. But the solution (20) is stable, while the vacuum state is not. In fact, when the initial state of the system is a mixture of the two phases: $c(x, t=0) = 0$ for $x < 0$, and $c(x, t=0) = c_{eq}$ for $x > 0$, say, then the stable phase invades the unstable phase. In the absence of drift, the front between the two phases propagates at the constant speed v (the birth rate) [23]. This system has been studied as a "noisy" analogue of the mean-field problem of Fisher waves [24]. Here we wish to study another inhomogeneous situation, where there is a perfectly absorbing trap at the origin, instead of the initial empty half-space.

As opposed to the Fisher problem, in the case of a trap the system arrives at a stationary state. This state

must be a non-equilibrium state, because the trap is irreversible (particles trapped in can't ever come out). As the trap depletes its immediate neighborhood, the depletion zone is continually replenished by a stream of particles from the stable phase which rush in at speed v, as in the Fisher wave problem. Suppose now that the particles are subject to a drift u away from the trap, then an interesting transition would take place as u is made larger than v: the depletion zone would grow faster than it could be replenished, and the stationary state would never be achieved! We wish to study this transition, and how the depletion zone is affected by the drift when $u < v$.

To derive the appropriate boundary condition, we turn back to the discrete representation. In the presence of a perfect trap at $n = 0$, Eq. (5) is limited to $0 < n < m$. The special equation for $n = 0$ is

$$\begin{aligned}\frac{\partial E_{0,m}}{\partial t} &= (\frac{D}{a^2} + \frac{u}{2a})(E_{0,m-1} - E_{0,m}) \\ &- (\frac{D}{a^2} - \frac{u}{2a})(E_{0,m} - E_{0,m+1}) \\ &+ (\frac{D}{a^2} - \frac{u}{2a})(E_{1,m} - E_{0,m}) \\ &- \frac{v}{a}(E_{0,m} - E_{0,m+1}) \ . \end{aligned} \tag{23}$$

Comparison to Eq. (5) yields the discrete boundary condition

$$E_{-1,m} = E_{0,m} \ , \tag{24}$$

which in the continuum limit becomes

$$\frac{\partial E(x,y;t)}{\partial x}|_{x=0} = 0 \ . \tag{25}$$

In addition, the boundary condition (13) is now replaced by

$$\lim_{y\to\infty} E(0,y;t) = 0 \ . \tag{26}$$

We are looking then for the solution to Eq. (19), confined to the wedge ($0 \le x \le y$), and which satisfies the boundary conditions (11), (12), (25), and (26). Following the method of separation of variables, assume $E(\eta,\xi) = \sum_\alpha A_\alpha f_\alpha(\eta) g_\alpha(\xi)$, then f_α and g_α satisfy the ODEs:

$$\frac{d^2 f_\alpha}{d\eta^2} - \omega \frac{df_\alpha}{d\eta} = +\alpha^2 f_\alpha \ , \tag{27}$$

$$\frac{d^2 g_\alpha}{d\xi^2} + \gamma \frac{dg_\alpha}{d\xi} = -\alpha^2 g_\alpha \ . \tag{28}$$

We find the solution by inspection: A good guess is that $\alpha^2 = 0$ would be part of it, since far away from the trap one expects convergence to the equilibrium state. However, $f_0 g_0$ fails to satisfy the boundary condition due to the trap, Eq. (25). Looking for the simplest possible way to mend this and to satisfy the remaining boundary conditions, we find that it is sufficient to consider just one additional component: $4\alpha^2 = \gamma^2 - \omega^2$. The final solution turns out to be

$$E_s(x,y) = e^{-\gamma(y-x)} + \frac{\gamma}{\omega} e^{-\gamma y}(e^{\omega y} - e^{\omega x}) \ . \tag{29}$$

Far away from the trap, as $x, y \to \infty$, this converges to the equilibrium result of Eq. (20).

From (14), we obtain the stationary concentration profile:

$$c_s(x) = \gamma[1 - e^{-(\gamma-\omega)x}] \ . \tag{30}$$

There is a depletion zone of size $(\gamma - \omega)^{-1} = D/(v - u)$ near the trap, and the concentration grows asymptotically to $c_{eq} = \gamma$ as $x \to \infty$. As the drift velocity u grows and approaches v, the depletion zone becomes larger and larger. In the limit $u \to v$ the depletion zone is infinite: from (29) we see that then $E_s \to 1$, *i.e.*, the stationary state is the vacuum (but it takes an infinite time to get there).

The IPDF is surprising. From (16) we get the conditional joint probability

$$P_s(x,y) = \gamma^2 e^{-\gamma(y-x)}[1 - e^{-(\gamma-\omega)x}] \ , \tag{31}$$

and so the forward IPDF is

$$p_s(x,y) = \gamma e^{-\gamma\xi} \ ; \qquad \xi \equiv y - x \ , \tag{32}$$

regardless of the drift. The notation chosen here emphasizes the fact that p_s is translationally invariant, in spite of the trap at the origin. In fact, the forward IPDF is exactly the same as in the *equilibrium* state (Eq. 22)!

The backward IPDF is

$$q_s(x,y) = \gamma \frac{e^{-\gamma\xi} - e^{-\omega\xi} e^{-(\gamma-\omega)y}}{1 - e^{-(\gamma-\omega)y}} \ ; \qquad \xi \equiv y - x \ . \tag{33}$$

Notice this time the dependence on the position of the given particle, y, as well as the dependence on the drift, and that the backward and forward IPDFs are *not* equal. Moreover, the backward IPDF does not normalize properly. The reason for that is that there is a finite chance that there are no particles between the particle at y and the trap; *i.e.*, the particle at y might be the nearest particle to the trap. The probability density for the distance of the nearest particle to the trap can be computed from the continuum limit of Eq. (3); $p_0(y) = -\partial E/\partial y|_{x=0}$, or

$$p_0(y) = \gamma \frac{\gamma - \omega}{\omega}[e^{-(\gamma-\omega)y} - e^{-\gamma y}] \ . \tag{34}$$

With this understanding, the proper normalization condition is

$$\int_0^y q(x,y)\, dx + c(y)^{-1} p_0(y) = 1 \ , \tag{35}$$

which is indeed met!

As a last remark, notice that all of the above results are also valid when the drift is *toward* the trap ($u < 0$). In this case the depletion zone shrinks as the drift's strength increases, and it vanishes in the limit of infinite drift.

V. SHIELDING

At first sight there seems to be a contradiction between the forward IPDF (Eq. 32) and the concentration profile (Eq. 30). How could it be that the distribution of distances between nearest particles is independent of location, while particles are sparser near the trap!? — The answer is that the forward IPDF is a *conditional* probability—dependent on the presence of the first particle at x. Thus, the unexpectedly small distance between particles in a sparse region is compensated by the rare likelihood of finding such pairs of nearest particles in the first place! Nevertheless, one can't help wondering what kind of distribution would explain the results of the previous section. The answer turns out to be surprisingly simple.

Suppose that the particles to the right of the trap are distributed just as in equilibrium, with the exception of the nearest particle to the trap. Assume further that the nearest particle to the trap is at distance z, with probability $p_0(z)$ (the same probability density as in Eq. 34). In this view, the effect of the trap is merely to create an empty gap between itself and the first particle—a gap which increases as the drift u approaches the critical value v. [It follows from Eq. (34) that the average distance to the first particle is $(2v-u)/(v-u)$.] Another way of looking at the suggested distribution is as if the nearest particle to the trap *shields* all the other particles from the effects of the trap! The proposed distribution is illustrated in Fig. 3.

We now show that this model reproduces the results of Section IV. All we need to do is to derive the empty interval probability $E(x,y)$ implied by the model, since everything else follows from it. $E(x,y)$ can attain one of three values—depending on the location of the endpoints of the (x,y) interval relative to the location of the nearest particle to the trap, z:

$$E(x,y) = \begin{cases} 1 & x < y < z \ , \\ 0 & x < z < y \ , \\ e^{-\gamma(y-x)} & z < x < y \ . \end{cases} \tag{36}$$

Therefore,

$$E(x,y) = \int_y^\infty p_0(z)\, dz + e^{-\gamma(y-x)} \int_0^x p_0(z)\, dz \ . \tag{37}$$

The result is exactly as E_s of Eq. (29)!

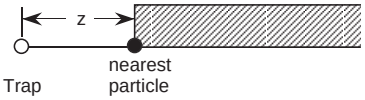

Figure 3. Schematic illustration of the shielding effect: The particles in the shaded area are distributed randomly and independently from each other, as in equilibrium. The gap z between the particles and the trap follows the probability density distribution $p_0(z)$.

So far, we have merely demonstrated that "shielding" is *consistent* with the exact results. A complete proof requires showing that the full hierarchy of n-point density-density correlation functions are the same as postulated by the shielding model. The problem of n-point correlation functions can be formulated exactly within the framework of the IPDF method [12]. With this method, it is rather straightforward to prove the shielding effect [25].

VI. REACTION-DIFFUSION EQUATION

Reaction-diffusion equations are one of the most valuable and widely used approaches to kinetics of reaction processes. The method posits the existence of a *mesoscopic* length scale within which the system is homogeneous and well mixed, and where the reaction rates can be accounted for as in classical rate equations. At longer length scales, variations in the concentration, $c(x,t)$, give rise to diffusion, which is modeled by a simple diffusion term. For example, the reaction-diffusion equation that applies to our model, in the absence of drift, is

$$\frac{\partial c(x,t)}{\partial t} = D' \frac{\partial^2 c}{\partial x^2} + k_1 c - k_2 c^2 \ , \tag{38}$$

together with the boundary condition:

$$c(0,t) = 0 \ , \tag{39}$$

which is imposed by the trap at the origin. D' is the effective diffusion constant, and k_1 and k_2 represent the effective rates of birth and coalescence of particles, respectively.

In spite of the popularity of reaction-diffusion equations it is not often appreciated that they are mere idealizations, yielding only approximate results. The reason for this misconception is twofold: (1) few exact solutions of reaction-diffusion models are available for comparison, and (2) the reaction-diffusion equations themselves are usually complicated enough that they cannot be solved in closed form, and so their consequences are not always clear. Diffusion-limited coalescence with a trap is a rare example where the stationary state is known exactly, and where also the corresponding reaction-diffusion equation may be solved exactly, at least in the case of zero drift [26]. We wish to compare the two solutions.

The exact steady state for zero drift, needed for the comparison, may be obtained from the results of Section IV. Taking the limit $w \to 0$ in Eqs. (29) and (30), we find

$$E_s(x,y) = e^{-\gamma(y-x)} + \gamma(y-x)e^{-\gamma y} \ , \tag{40}$$

and

$$c_s(x) = \gamma(1 - e^{-\gamma x}) \ . \tag{41}$$

Regarding the reaction-diffusion equation, Eq. (38), our first concern is to identify the constants D', k_1, and k_2. We note first that

$$D' = D \,, \tag{42}$$

since in the absence of reactions (when $k_1, k_2 = 0$) the particles perform simple diffusion, characterized by the diffusion constant D—the same D as in the hopping rate D/a^2 of the microscopic rules. Furthermore, in the continuum limit the model's only physical parameters relevant to its kinetics are the diffusion constant D (of dimension L^2/T; $L \equiv$ length, and $T \equiv$ time) and the birth rate v (dimension L/T). Therefore, the only way to produce the required dimensions of k_1 $(1/T)$ and k_2 (L/T) is by having $k_1 \sim v^2/D$ and $k_2 \sim v$. Finally, consider the stationary solution of Eq. (38) in an infinite system without the trap: $c_{eq} = k_1/k_2$. To conform with the exact solution of (21) we must have $k_1/k_2 = v/D$. Thus,

$$k_1 = \beta \frac{v^2}{D} \;; \qquad k_2 = \beta v \,, \tag{43}$$

where β is a constant.

The stationary solution to Eq. (38) with the trap—the boundary condition (39)—is

$$\frac{c_s(x)}{c_\infty} = \frac{3}{2} \tanh^2 \left(\sqrt{\frac{k_1}{3D}} x + \tanh^{-1} \sqrt{\frac{1}{3}} \right) - \frac{1}{2} \,, \tag{44}$$

where $c_\infty = k_1/k_2 = v/D$ is the concentration of particles infinitely far away from the trap. The concentration profile described by Eq. (44) looks similar to the exact result of Eq. (41). One could now use different criteria to determine the value of the fitting parameter β. Demanding the correct asymptotic behavior far away from the trap; $\lim_{x\to\infty} \ln[1 - c_s(x)/c_{eq}]/x = -v/D$, we get $\beta = 3/4$. On the other hand, if we require the correct behavior close to the trap; $(\partial c_s/\partial x)_{x=0} = (v/D)^2$, we get $\beta = 9/4$. Clearly, it is impossible to find a value of β that reproduces the short range behavior and the long range behavior simultaneously. In Fig. 4 we show the results of a least square fit in the range $0 \le (v/D)x \le 5$, which is achieved with $\beta = 1.27$.

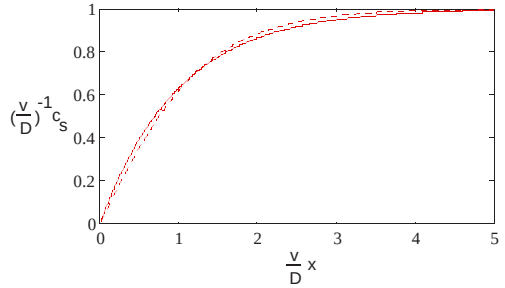

Figure 4. Comparison of the exact analytic concentration profile (solid line) to the prediction of the reaction-diffusion equation (broken line). Shown is the result of a best fit, achieved with $\beta = 1.27$.

VII. DISCUSSION

We have solved the one-dimensional problem of diffusion-limited reversible coalescence with a trap, and with a background drift, exactly. The system exhibits a dynamical phase transition in its long-time asymptotic steady state, which is controlled by the strength of the drift away from the trap. As the drift increases the depletion zone near the trap grows larger, until when the drift crosses a critical threshold and the depletion zone becomes infinitely wide; the system is then empty.

A very intriguing prediction of the exact solution is the distribution of distances between any given particle and its nearest neighbor to the right (the forward IPDF), which turns out to be exactly the same as in equilibrium—as in the system without the trap—and independent of the drift! This is explained by a "shielding" effect: the nearest particle to the trap effectively shields the rest of the particles from the trap's influence. The trap and background drift affect only the width of the gap between the trap and the nearest particle.

We have also contrasted the exact solution, in the absence of drift, with the alternative, traditional approach of reaction-diffusion equations. Our model is a nontrivial example where both the true kinetics, as well as the solution to the model's reaction-diffusion equation, are known exactly. Comparing the two solutions we were able to relate the effective rates of the reaction-diffusion equation to the microscopic rates of the underlying process, without appealing to renormalization group techniques.

There remain several interesting open questions. The exact solution of Section IV is basically an inspired guess. It would be useful to develop a more formal derivation method—one that would allow further analysis of different generalizations of the problem at hand. Other open problems include the question of transient behavior. For example, beyond the transition point, when the drift exceeds the critical value of $u_c = v$, it takes an infinite time for the system to achieve the empty steady state. What is the exact time dependence at different points of the phase diagram? —What is the mean-field critical dimension beyond which the reaction-diffusion equation becomes exact? Previous work on a closely related problem (Fisher waves [24]) has suggested that $d_c = 3$, but it was based on computer simulations of an "infinite" system and the results were controversial. The bounding of our present model by the trap at the origin may offer a better alternative for numerical studies. —What is the prediction of the reaction-diffusion equation formulation when drift is included? How well is the dynamical phase transition captured in this approximation? These and similar issues will be the subject of future research.

ACKNOWLEDGMENTS

I thank L. Glasser, P. Krapivsky, V. Privman, S. Redner, and L. Schulman for valuable discussions.

---

[1] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).

[2] H. Haken, *Synergetics* (Springer-Verlag, Berlin, 1978).

[3] G. Nicolis and I. Prigogine, *Self-Organization in Non-Equilibrium Systems* (Wiley, New York, 1980).

[4] T. M. Liggett, *Interacting Particle Systems* (Springer-Verlag, New York, 1985).

[5] S. A. Rice, *Diffusion-Limited Reactions* (Elsevier, Amsterdam, 1985).

[6] K. Kang and S. Redner, Phys. Rev. A **32**, 435 (1985); V. Kuzovkov and E. Kotomin, Rep. Prog. Phys. **51**, 1479 (1988).

[7] J. Stat. Phys. Vol. **65**, nos. 5/6 (1991); this issue contains the proceedings of a conference on *Models of Non-Classical Reaction Rates*, which was held at NIH (March 25–27, 1991) in honor of the 60th birthday of G. H. Weiss.

[8] K. J. Laidler, *Chemical Kinetics* (McGraw-Hill, New York, 1965).

[9] S. W. Benson, *The Foundations of Chemical Kinetics* (McGraw-Hill, New York, 1960).

[10] D. ben-Avraham, M. A. Burschka, and C. R. Doering, J. Stat. Phys. **60**, 695 (1990).

[11] D. ben-Avraham, Mod. Phys. Lett. B **9**, 895 (1995); D. ben-Avraham, in *Nonequilibrium Statistical Mechanics in One Dimension*, V. Privman, ed., pp 29–50 (Cambridge University Press, 1997).

[12] C. R. Doering, Physica A **188**, 386 (1992).

[13] H. Hinrichsen, K. Krebs, and M. P. Pfannmüller, J. Stat. Phys. **78**, 1429 (1995); B. Wehefritz, K. Krebs, and M. P. Pfannmüller, J. Stat. Phys. **78**, 1471 (1995); H. Hinrichsen, K. Krebs, ands I. Peschel, Z. Phys. B **100**, 105 (1996).

[14] M. Henkel, E. Orlandini, and G. M. Schütz, J. Phys. A **28**, 6335 (1995); M. Henkel, E. Orlandini, and J. Santos, Ann. Phys. (NY) **259**, 163 (1997).

[15] H. Simon, J. Phys. A **28**, 6335 (1995).

[16] D. Balboni, P.-A. Rey, and M. Droz, Phys. Rev. E **52**,6220 (1995); P.-A. Rey and M. Droz, J. Phys. A **30**, 1101 (1997).

[17] M. Bramson and D. Griffeath, Ann. Prob. **8**, 183 (1980); Z. Wahrsch. Geb. **53**, 183 (1980).

[18] D. C. Torney and H. M. McConnell, Proc. R. Soc. Lond. A **387** 147 (1983).

[19] J. L. Spouge, Phys. Rev. Lett. **60**, 871 (1988).

[20] H. Takayasu, I. Nishikawa and H. Tasaki, Phys. Rev. A **37** 3110 (1988).

[21] V. Privman, Phys. Rev. E **50**, 50 (1994); Mod. Phys. Lett. B **8**, 143 (1994); V. Privman, A.M.R. Cadilhe, and M.L. Lawrence, J. Stat. Phys. **81**, 881 (1995); Phys. Rev. E **53**, 739 (1996);

[22] Our notation here differs from previous work: we take the birth rate to be v/a rather than $v/2a$, to achieve a more aesthetic form of the final result.

[23] C. R. Doering, M. A. Burschka, and W. Horsthemke, J. Stat. Phys. **65**, 953 (1991).

[24] J. Riordan, C. R. Doering, and D. ben-Avraham, Phys. Rev. Lett. **75**, 565 (1995).

[25] A similar proof can be found in D. ben-Avraham, *Fisher Waves in the Diffusion-Limited Coalescence Process* $A + A \rightleftharpoons A$, preprint: cond-mat/9805180. Submitted to Phys. Lett. A.

[26] D. ben-Avraham, *Diffusion-Limited Coalescence,* $A + A \rightleftharpoons A$*, with a Trap*, preprint: cond-mat/9802214. Submitted to Phys. Rev. E.